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[19. ABSTRACT]

Combining  $\text{P}(\text{SiMe}_3)_3$  or  $\text{As}(\text{SiMe}_3)_3$  with  $\text{Ph}_2\text{InCl}$  in a 1:1 mole ratio results in the elimination of  $\text{Me}_3\text{SiCl}$  via a dehalosilylation reaction to yield  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I) and  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II), respectively. Both I and II crystallize in the monoclinic system but they are not isomorphous. Crystals of compound I belong to space group  $P2_1/c$  with  $a = 10.691(1)$ ,  $b = 19.821(2)$ ,  $c = 11.512(1)$  Å,  $\beta = 113.34(1)^\circ$ ,  $V = 2239.8(8)$  Å<sup>3</sup>, and  $D_{\text{calc.}} = 1.324$  g cm<sup>-3</sup> for  $Z = 2$ . Compound II crystallizes in space group  $P2_1/n$  with  $a = 16.248(1)$ ,  $\beta = 20.285(1)$ ,  $c = 13.887(1)$  Å,  $b = 90.12(1)^\circ$ ,  $V = 4577.0(8)$  Å<sup>3</sup>, and  $D_{\text{calc.}} = 1.423$  g cm<sup>-3</sup> for  $Z = 4$ . Full-matrix least-squares refinement based on 2765 (I) and 3625 (II) reflections with  $I > 3\sigma(I)$ , respectively, converged at  $R = 0.038$  ( $R_w = 0.050$ ) for I and  $R = 0.040$  ( $R_w = 0.048$ ) for II. The  $(\text{InP})_2$  core of dimer I is planar whereas in dimer II the  $(\text{InAs})_2$  ring is slightly puckered.

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SYNTHESIS AND MOLECULAR STRUCTURES OF  $[\text{Ph}_2\text{InE}(\text{SiMe}_3)_2]_2$  ( $E = \text{P or As}$ )

by

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DEHALOSILYLATION REACTIONS INVOLVING  $E(\text{SiMe}_3)_3$  AND  
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 $[\text{Ph}_2\text{InE}(\text{SiMe}_3)_2]_2$  ( $E = \text{P}$  or  $\text{As}$ ).

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**Abstract**— Combining  $\text{P}(\text{SiMe}_3)_3$  or  $\text{As}(\text{SiMe}_3)_3$  with  $\text{Ph}_2\text{InCl}$  in a 1:1 mole ratio results in the elimination of  $\text{Me}_3\text{SiCl}$  via a dehalosilylation reaction to yield  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I) and  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II), respectively. Both I and II crystallize in the monoclinic system but they are not isomorphous. Crystals of compound I belong to space group  $P2_1/c$  with  $a = 10.691(1)$ ,  $b = 19.821(2)$ ,  $c = 11.512(1)$  Å,  $\beta = 113.34(1)^\circ$ ,  $V = 2239.8(8)$  Å<sup>3</sup>, and  $D_{\text{calc.}} = 1.324$  g cm<sup>-3</sup> for  $Z = 2$ . Compound II crystallizes in space group  $P2_1/n$  with  $a = 16.248(1)$ ,  $\beta = 20.285(1)$ ,  $c = 13.887(1)$  Å,  $b = 90.12(1)^\circ$ ,  $V = 4577.0(8)$  Å<sup>3</sup>, and  $D_{\text{calc.}} = 1.423$  g cm<sup>-3</sup> for  $Z = 4$ . Full-matrix least-squares refinement based on 2765 (I) and 3625 (II) reflections with  $I > 3\sigma(I)$ , respectively, converged at  $R = 0.038$  ( $R_w = 0.050$ ) for I and  $R = 0.040$  ( $R_w = 0.048$ ) for II. The  $(\text{InP})_2$  core of dimer I is planar whereas in dimer II the  $(\text{InAs})_2$  ring is slightly puckered.

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The quest for suitable single-source precursors to ceramic and/or electronic III-V materials in previous years has resulted in a large number of fundamental reports concerning the structural aspects and reactivities of these compounds.<sup>1,2</sup> Elucidation of this basic

chemistry is paramount to the understanding of the nature of the factors that influence the correct design and fabrication of such materials. Research in our laboratory has primarily centered on the use of silylarsines and, of late, silylphosphines in dehalosilylation reactions with a dialkyl group III halide or group III trihalide. These reactions eliminate a silyl halide thus forming a III-V bond.<sup>1,3</sup> This line of investigation has proven to be very fruitful in that a variety of compounds containing  $\overline{\text{MEME}}$  ( $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ ;<sup>4-7</sup>  $\text{M} = \text{In}$ ,  $\text{E} = \text{P}^8$  or  $\text{As}$ ;<sup>9</sup>) and  $\overline{\text{MEMCl}}$  ( $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ ;<sup>4,6,7</sup> or  $\text{P}$ ;<sup>10</sup>  $\text{M} = \text{In}$ ,  $\text{E} = \text{P}^8$  or  $\text{As}$ ;<sup>9</sup>) cores have been isolated. From the latter compounds, the possibility of replacing the chlorine atom with other functionalities exists.<sup>11</sup> Currently, for the case of compounds with cores consisting of  $\overline{\text{MEME}}$  ( $\text{M} = \text{In}$ ,  $\text{E} = \text{P}$  or  $\text{As}$ ) rings, we have only employed this dehalosilylation methodology to  $(\text{Me}_3\text{SiCH}_2)_2\text{InCl}$ .<sup>8,9</sup> Herein we report our further explorations into this area with the synthesis and structural characterization of  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I) and  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II).

## EXPERIMENTAL

### Synthesis

All manipulations were performed using general Schlenk, dry box, and/or high vacuum techniques. Solvents (including those for NMR spectra) were appropriately dried, distilled under argon, and degassed prior to use. Literature methods were used to prepare  $\text{Ph}_3\text{In}$ ,<sup>12</sup>  $\text{P}(\text{SiMe}_3)_3$ ,<sup>13</sup> and  $\text{As}(\text{SiMe}_3)_3$ .<sup>14</sup>  $\text{In(III)}$  chloride was purchased from Alfa Products, Ward Hill, MA, and purified by sublimation.  $\text{Ph}_2\text{InCl}$  was prepared *via* the equilibration of  $\text{Ph}_3\text{In}$  and  $\text{In(III)}$  chloride in refluxing toluene in a 2:1 mole ratio and purified by recrystallization.  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were obtained on a Varian XL-300 at 300.0, 75.4, and 121.4 MHz, respectively.  $^1\text{H}$  and  $^{13}\text{C}$  spectra were referenced to TMS *via* the residual protons or carbons of  $\text{C}_6\text{D}_6$ .  $^{31}\text{P}$  spectra were referenced to external 80%  $\text{H}_3\text{PO}_4$  at  $\delta$  0.00 ppm. Melting points (uncorrected) were taken in sealed capillaries (Thomas-Hoover Uni-melt). Elemental analyses were performed by  $\alpha/\alpha$

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E + R Microanalytical Laboratory, Inc., Corona, N Y. Single crystal X-ray data were collected on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu-K $\alpha$  radiation.

(1)  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I)

Inside the dry-box, a one necked 250 mL round-bottom flask equipped with a Teflon valve was charged with pentane (15 cm<sup>3</sup>) and  $\text{Ph}_2\text{InCl}$  (0.250 g, 0.82 mmol) furnishing a white suspension to which was added dropwise  $\text{P}(\text{SiMe}_3)_3$  (0.206 g, 0.82 mmol) in pentane (20 cm<sup>3</sup>). The resulting milky mixture was placed in a sonicating water bath and allowed to react for 48 h during which it became pale yellow. The volatiles were removed *in vacuo*, and the crude product was dissolved in warm pentane (15 cm<sup>3</sup>). Upon cooling to -15° for several days, colourless, air-sensitive crystals of I formed; 0.224 g, 61.2% yield, mp. 205 - 240°C (dec). Found: C, 48.40; H, 6.32. Calc. for  $\text{C}_{36}\text{H}_{56}\text{In}_2\text{P}_2\text{Si}_4$ : C, 48.61; H, 6.29. <sup>1</sup>H NMR:  $\delta$  0.34 (t, 36 H,  $\text{SiMe}_3$  ( $J_{\text{P-H}} = 2.7$  Hz)), 7.17 (t, 4 H, *para*- $\text{C}_6\text{H}_5$ ), 7.26 (t, 8H, *meta*- $\text{C}_6\text{H}_5$ ), 7.80 (d, 8H, *ortho*- $\text{C}_6\text{H}_5$ ). <sup>13</sup>C {<sup>1</sup>H} NMR:  $\delta$  4.79 [t,  $\text{SiMe}_3$  ( $J_{\text{P-C}} = 4.7$  Hz)], [127.63 - 129.17 (m,  $\text{C}_6\text{H}_5$ ) partially obscured by solvent], 139.23 (s,  $\text{C}_6\text{H}_5$ ). <sup>31</sup>P {<sup>1</sup>H} NMR:  $\delta$  -221.59 (s).

(2)  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II)

In a manner similar to that employed for the preparation of I,  $\text{Ph}_2\text{InCl}$  (0.250 g, 0.82 mmol) in 15 cm<sup>3</sup> of pentane and  $\text{As}(\text{SiMe}_3)_3$  (0.243 g, 0.82 mmol) in pentane (20 cm<sup>3</sup>) were combined. The resulting milky mixture was stirred for 48 h at room temperature giving a yellow solution. The volatiles were removed *in vacuo* and the crude product was dissolved in warm pentane (15 cm<sup>3</sup>). Upon cooling to -15° for several days, colourless, air-sensitive crystals of II formed; 0.141 g, 35.0% yield, mp. 185-190 °C (dec to orange liquid). Found: C, 44.49; H, 6.09. Calc. for  $\text{C}_{36}\text{H}_{56}\text{As}_2\text{In}_2\text{Si}_4$ : C, 44.09; H, 5.76. <sup>1</sup>H NMR:  $\delta$  0.35 (s, 36 H,  $\text{SiMe}_3$ ) 7.18 (t, 4 H, *para*- $\text{C}_6\text{H}_5$ ), 7.29 (t, 8H, *meta*- $\text{C}_6\text{H}_5$ ), 7.85

(d, 8H, *ortho*-C<sub>6</sub>H<sub>5</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR: δ 5.00 (s, SiMe<sub>3</sub>), [127.80 (s, C<sub>6</sub>H<sub>5</sub>), 128.12 (s, C<sub>6</sub>H<sub>5</sub>) partially obscured by solvent], 139.00 (s, C<sub>6</sub>H<sub>5</sub>).

#### *X-ray structural solution and refinement*

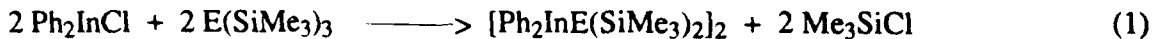
Colourless crystals of **I** and **II** were mounted inside flame-sealed 0.6 mm thin-walled glass capillaries under an inert argon atmosphere. Oscillation and Weissenberg photographs provided preliminary unit cell parameters and space group information. The monoclinic space groups *P*2<sub>1</sub>/*c* for **I** and *P*2<sub>1</sub>/*n* (alternative setting of *P*2<sub>1</sub>/*c*) for **II** were established unequivocally from the Laue symmetry and systematic absences. Crystallographic data are summarized in Table 1. Intensity data (+*h*, +*k*, ±*l*; 4832 reflections, θ<sub>max</sub> = 75° for **I**; 8025 reflections, θ<sub>max</sub> = 65° for **II**), recorded on an Enraf-Nonius CAD-4 diffractometer (Cu-Kα radiation, λ = 1.5418 Å, graphite monochromator), were corrected for the usual Lorentz and polarization effects; empirical absorption corrections (derived from ψ-scans) were also applied. Equivalent reflections were averaged leaving 4598(**I**) and 7734(**II**) out of which those 2765 and 3625, respectively, with *I* > 3.0σ(*I*) were retained for the analyses. With two formula units per unit cell, dimer **I** must lie on a crystallographic centre of symmetry. For **II**, on the other hand, the unit cell contains four dimers that may either occupy general positions or two crystallographically independent dimers must lie on centres of symmetry. Initial indium atom coordinates for **I** were derived from a Patterson map. Approximate indium and arsenic coordinates for **II**, obtained from an *E*-map (MULTAN11/82), indicated that the molecules lay in general positions with no crystallographically-imposed symmetry. The remaining non-hydrogen atoms of **I** and **II** were located in a series of weighted *F*<sub>o</sub> and difference Fourier syntheses phased successively by an increasing number of atoms. Several rounds of full-matrix least-squares adjustment of atomic positional and thermal parameters (at first isotropic, then anisotropic) followed. In the later iterations, hydrogen atoms were incorporated at their calculated positions (C-H = 1.05 Å) and an extinction correction was included as a variable. The parameter refinements converged at *R* = 0.038

( $R_w = 0.050$ ) for **I** and  $R = 0.040$  ( $R_w = 0.048$ ) for **II**. Final difference Fourier syntheses revealed no unusual features [max.  $\Delta\rho(e/\text{\AA}^3)$ : 0.54 (**I**) and 0.56 (**II**), both in the vicinity of the In atom]. The solid-state structures of **I** and **II**, with their atom numbering schemes, are illustrated in Figs. 1 and 2, respectively. Selected bond lengths and bond angles are listed in Tables 2 and 3. Crystallographic calculations were performed using the Enraf-Nonius Structure Determination Package<sup>15</sup> on PDP11/44 and MicroVAX computers. For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref. 16. In the least-squares iterations,  $\text{SwD}^2$  [ $w = 1/s^2(|F_o|)$ ,  $D = (|F_o| - |F_c|)$ ] was minimized. Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles and crystal data have been deposited with the Cambridge Crystallographic Data Centre.

## RESULTS AND DISCUSSION

We have previously demonstrated the utility of dehalosilylation reactions between an organogroup III halide and a silylarsine<sup>1</sup> or silylphosphine<sup>8,10</sup> to form III-V bonds. Our initial efforts in pursuit of compounds possessing In-E bonds (E = As or P) involved only the reaction of organoindium species bearing the  $\text{Me}_3\text{SiCH}_2$  group,<sup>8,9</sup> an organic substituent that was chosen because of its steric bulk and relative stability. In an effort to ascertain the viability of our methodology for other systems, we have begun to explore the use of different organic substituents at the organoindium centre. We now report the synthesis, characterizations, and X-ray structures of two new compounds containing the In-E bond (E = P or As),  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (**I**) and  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (**II**).

The 1:1 mole ratio reaction of  $\text{Ph}_2\text{InCl}$  with  $\text{E}(\text{SiMe}_3)_3$  (E = P or As) at room temperature in pentane affords **I** and **II**, respectively, via a dehalosilylation reaction (eq 1).





Compounds **I** and **II** are the second examples of dimeric In-P or In-As species to be prepared in our laboratory through the elimination of  $\text{Me}_3\text{SiCl}$ , with  $[(\text{Me}_3\text{SiCH}_2)_2\text{InP}(\text{SiMe}_3)_2]_2$  (**III**)<sup>8</sup> and  $[(\text{Me}_3\text{SiCH}_2)_2\text{InAs}(\text{SiMe}_3)_2]_2$  (**IV**)<sup>9</sup> constituting the first. Subsequent to **III** and **IV** being reported, Theopold and co-workers demonstrated that  $[\text{C}_5\text{Me}_5(\text{Cl})\text{InP}(\text{SiMe}_3)_2]_2$  (**V**)<sup>17</sup> results from a like reaction. As with **III**, **IV**, and **V**, the core fragment of **I** consists of planar four-membered  $(\text{InP})_2$  ring whereas in **II** the  $(\text{InAs})_2$  ring is slightly puckered (*vide infra*). The  $^1\text{H}$ ,  $^{13}\text{C}$ , and for **I**,  $^{31}\text{P}$  room temperature NMR spectra for each compound are consistent with their solid-state structures. The dimeric nature of **I** is clearly demonstrated by the virtual coupling of the ring phosphorus atoms with the hydrogen and carbon atoms of the trimethylsilyl substituents at the phosphorus centre. This coupling gives rise to a triplet for these groups in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. At room temperature no evidence of solution fluxionality has been observed for either **I** or **II**.

Compound **I** crystallizes in the monoclinic space group  $P2_1/c$  with the two dimers in the unit cell lying on crystallographic centres of symmetry and accordingly the  $(\text{InP})_2$  ring is required to be strictly planar. The In-P bond lengths are both  $2.612(1) \text{ \AA}$ , a distance which is distinctly shorter than the mean of  $2.655 \text{ \AA}$  in **III**, reflecting the less sterically demanding nature of the phenyl substituents in **I** versus the much bulkier  $\text{Me}_3\text{SiCH}_2$  moieties in **III**. The mean P-Si bond length of  $2.262 \text{ \AA}$  in **I** is similar to the mean of  $2.255 \text{ \AA}$  in **III**. Bond angles in the  $(\text{InP})_2$  core of **I** [ $\text{In-P-In} = 92.97(4)^\circ > \text{P-In-P} = 87.03(4)^\circ$ ] are similar to and differ in the same sense as corresponding angles in **III** [ $93.6(1)^\circ$ ,  $86.4^\circ$  (mean)] and **V** [ $92.2(1)^\circ$ ,  $87.8(1)^\circ$ ]. The C-In-C angle at  $105.7(2)^\circ$  in **I** is very much smaller than the mean of  $123.2^\circ$  in **III** where the considerable enlargement from an approximately tetrahedral value may be ascribed at least in part to the greater steric crowding by the geminal  $\text{Me}_3\text{SiCH}_2$  substituents. It is relevant to note that the larger the exocyclic bond angle subtended at an opposite pair of ring atoms in four-membered rings is, the greater the steric compression exerted on substituents at the other ring centres is. It

is therefore not surprising to find that the Si-P-Si angle of  $108.3(1)^\circ$  in **I** is slightly larger than that of  $105.7(2)^\circ$  in **III**. In contrast to the situations in  $[\text{In}(\text{2,4,6-trimethylphenyl})_2\text{I}]_2$ ,<sup>18</sup>  $(\text{Ph}_2\text{InOSiMe}_3)_2$ ,<sup>19</sup> and  $[\text{Ph}_2\text{GaAs}(\text{CH}_2\text{SiMe}_3)_2]_2$ <sup>5</sup> where one of the phenyl ring planes approximately eclipses one of the four-membered ring bonds while the other is in a bisecting orientation or in  $\text{Ph}_2\text{GaAs}(\text{SiMe}_3)_2\text{Ga}(\text{Ph})_2\text{Cl}$ <sup>6</sup> where all are in approximately eclipsing orientations, both of the phenyl rings in **I** are rotated moderately away from either the eclipsing or the bisecting orientation [torsion angles:  $\text{P-In-C}(31)\text{-C}(36) = 36.4(6)^\circ$ ,  $\text{P'-In-C}(31)\text{-C}(32) = -49.5(5)^\circ$ ;  $\text{P'-In-C}(41)\text{-C}(42) = -22.5(6)^\circ$ ,  $\text{P-In-C}(41)\text{-C}(42) = 78.1(6)^\circ$ ] to minimize intramolecular non-bonded interactions with the proximal SiMe<sub>3</sub> substituents. The In atom lies close to the C(41)-C(46) least-squares plane ( $\Delta = 0.013 \text{ \AA}$ ) but is displaced significantly ( $\Delta = 0.108 \text{ \AA}$ ) from that through the other phenyl ring atoms [C(31)-C(36)]. Substituent crowding is also indicated in the highly significant differences between the exocyclic bond angles at the *ipso* carbon atoms [ $\text{In-C}(31)\text{-C}(36) = 125.3(5)^\circ > \text{In-C}(31)\text{-C}(32) = 118.2(5)^\circ$ ;  $\text{In-C}(41)\text{-C}(42) = 127.9(5)^\circ > \text{In-C}(41)\text{-C}(46) = 114.5(5)^\circ$ ].

Crystals of dimer **II** also belong to the monoclinic system but they are not isomorphous with those of **I**. Compound **II** crystallizes in space group  $P2_1/n$  with four molecules occupying the general positions. In contrast to the planar  $(\text{InAs})_2$  ring in **I**, in **II** the ring is very slightly puckered [ $\text{As}(1)\text{-In}(1)\text{-As}(2)/\text{As}(1)\text{-In}(2)\text{-As}(2)$  dihedral angle =  $6.0^\circ$ ]. The mean In-As bond length at  $2.686 \text{ \AA}$  in **II** is significantly shorter than the value of  $2.728 \text{ \AA}$  in the planar ring of **IV**; the difference between these distances ( $\Delta = 0.042 \text{ \AA}$ ), which is essentially the same as that between the corresponding bonds ( $\Delta = 0.043 \text{ \AA}$ ) in the phosphorus analogues **I** and **III**, again may be ascribed principally to the different steric demands of the geminal substituents,  $\text{Ph} \ll \text{Me}_3\text{SiCH}_2$ . Endocyclic bond angles [ $\text{In-As-In} = 93.48^\circ(\text{mean}) > \text{As-In-As} = 86.36^\circ(\text{mean})$ ] in **II** lie close to the corresponding values for **IV** [ $94.57(5)^\circ$ ,  $85.43^\circ(\text{mean})$ ]. The mean As-Si bond length [ $2.355 \text{ \AA}$ ] and the mean Si-As-Si bond angle [ $106.2^\circ$ ] in **II** do not differ significantly from those in **IV** [ $\text{As-Si} = 2.348 \text{ \AA}(\text{mean})$ ,  $\text{Si-As-Si} = 105.4(2)^\circ$ ]. In addition, the mean In-C bond length at  $2.18 \text{ \AA}$

in **II** is the same as that in **I** (2.182 Å). The mean of the C-In-C angles at 108.5° in **II** is slightly larger than that of 105.7(2)° in **I** whereas it is much smaller than the mean of 125.4° in **IV** which has the bulky Me<sub>3</sub>SiCH<sub>2</sub> substituents at In. With the reduced symmetry of **II** versus **I**, the dispositions of the phenyl rings with respect to the As-In bonds show more variation [torsion angles: As(2)-In(1)-C(1)-C(2) = -27(1)°, As(1)-In(1)-C(1)-C(6) = 58(1)°; As(1)-In(1)-C(7)-C(12) = 41(1)°, As(2)-In(1)-C(7)-C(2) = -59(1)°; As(1)-In(2)-C(13)-C(14) = 15(1)°, As(2)-In(2)-C(13)-C(18) = -72(1)°; As(2)-In(2)-C(19)-C(24) = -25(1), As(1)-In(2)-C(19)-C(24) = 73(1)°]. The In atom lies out of each of the phenyl ring planes [D = 0.070 Å, 0.108 Å, 0.151 Å, 0.156 Å, respectively, from the C(1)-C(6), C(7)-C(12), C(13)-C(18) and C(19)-C(24) least-squares planes]. In common with **I**, exocyclic bond angle deformation at the *ipso* carbon centres is also present in **II** [In(1)-C(1)-C(2) = 123(1)° > In(1)-C(1)-C(6) = 119(1)°; In(1)-C(7)-C(12) = 125(1)° > In(1)-C(7)-C(8) = 117(1)°; In(2)-C(13)-C(14) = 126(1)° > In(2)-C(13)-C(18) = 119(1)°; In(2)-C(19)-C(24) 125(1)° > In(2)-C(19)-C(20) = 119(1)°] to aid in the minimization of intramolecular non-bonded interactions.

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Captions to Figures

Fig 1. ORTEP diagram (30% probability ellipsoids) of the solid-state structure of  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I); primed atoms are related to the unprimed atoms by a crystallographic centre of symmetry. Hydrogen atoms have been omitted for clarity.

Fig 2. ORTEP diagram (30% probability ellipsoids) of the solid-state structure of  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II). Hydrogen atoms have been omitted for clarity.

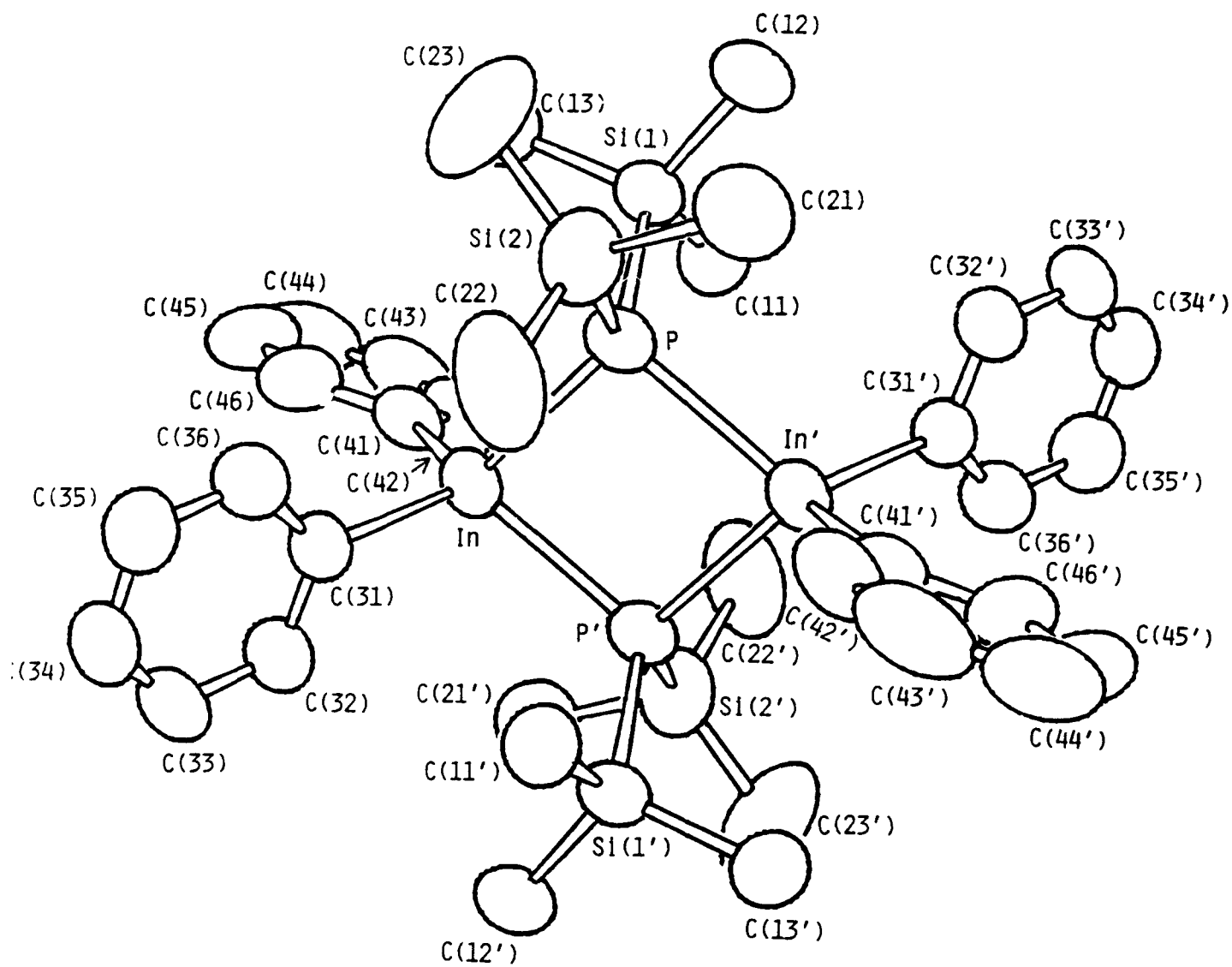


Fig. 1

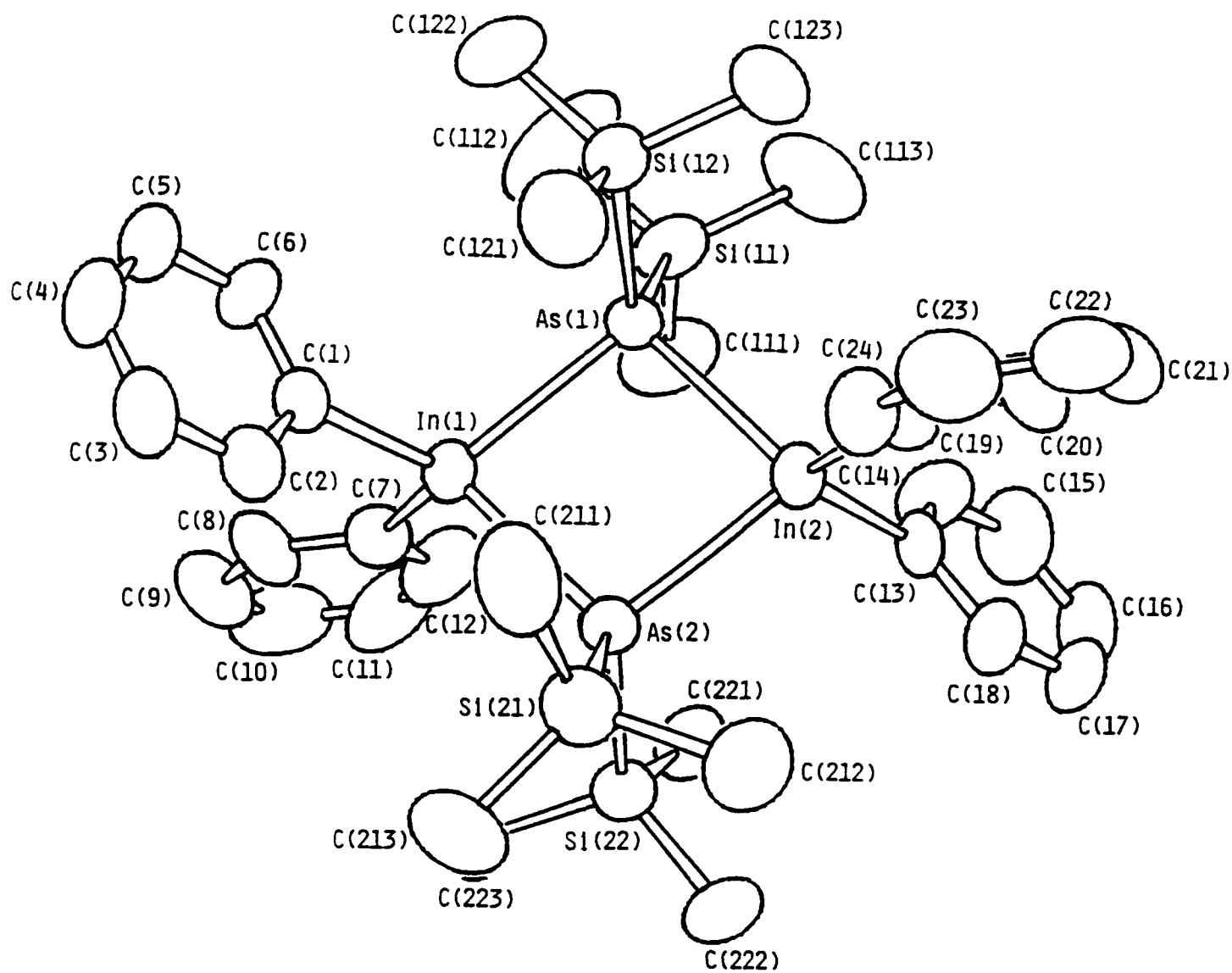


Fig. 2

Table 1. Crystallographic data and summary of data collection and refinement for  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I) and  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II)

	(I)	(II)
molecular formula	$\text{C}_{36}\text{H}_{56}\text{In}_2\text{P}_2\text{Si}_4$	$\text{C}_{36}\text{H}_{56}\text{As}_2\text{In}_2\text{Si}_4$
formula weight	892.78	980.68
crystal system	monoclinic	monoclinic
space group	$P2_1/c(C_{2h}^5)$	$P2_1/n(C_{2h}^5)$
$a$ (Å)	10.691(1)	16.248(1)
$b$ (Å)	19.821(2)	20.285(1)
$c$ (Å)	11.512(1)	13.887(1)
$\beta$ (°)	113.34(1)	90.12(1)
no. of orient. refls; $\theta$ , deg, range	25; 36-40	25; 36-40
$V$ (Å <sup>3</sup> )	2239.8(8)	4577.0(8)
$Z$	2	4
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.324	1.423
temp (K)	296	296
crystal dimensions (mm)	0.18 x 0.18 x 0.40	0.21 x 0.23 x 0.28
$T_{\text{max}}:T_{\text{min}}$	1.00:0.68	1.00:0.76
radiation (wavelength)	Cu- $K\alpha$ (1.5418 Å)	Cu- $K\alpha$ (1.5418 Å)
$\mu$ (cm <sup>-1</sup> )	103.1	110.4
scan type	$\omega$ -2 $\theta$	$\omega$ -2 $\theta$
scan width (°)	$0.80 + 0.14\tan\theta$	$0.70 + 0.14\tan\theta$
$\theta_{\text{max}}$ (°)	75	65
intensity control reflns	131,232,332,421	132,212,331,412
variation; repeat time (h)	<2%; 2	<1%; 2



Table 1(cont)

no of rflns recorded	4832 (+h,+k, <u>±</u> l)	8025 (+h,+k, <u>±</u> l)
no of non-equiv refls	4598	7734
<i>R</i> (merge)	0.029 on <i>I</i>	0.034 on <i>I</i>
no of rflns retained, <i>I</i> > 3.0σ( <i>I</i> )	2765	3625
no of parameters refined	200	398
extinction correction	6.8(4) x 10 <sup>-7</sup>	1.7(1) x 10 <sup>-7</sup>
<i>R</i> ( <i>F</i> ), <i>R</i> <sub>w</sub> ( <i>F</i> ) <sup>a</sup>	0.038, 0.050	0.040, 0.048
goodness-of-fit <sup>b</sup>	1.25	1.17
max shift; esd in final least-squares cycle	0.02	0.01
final Δρ(e/Å <sup>3</sup> ) max; min	0.54; -0.55	0.56; -0.56

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<sup>a</sup> $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ ;  $R_w = [\Sigma w (|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$ ;

$\Sigma w \Delta^2 [w = 1/\sigma^2(|F_o|), \Delta = (|F_o| - |F_c|)]$  was minimized.

<sup>b</sup> Goodness-of-fit =  $[\Sigma w \Delta^2 / (N_{\text{observations}} - N_{\text{parameters}})]^{1/2}$ .

Table 2. Selected bond lengths (Å) and bond angles (°), with ESD's in parentheses, for  $[\text{Ph}_2\text{InP}(\text{SiMe}_3)_2]_2$  (I).

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(a) Bond lengths			
P-In	2.612(1)	In-C(31)	2.178(6)
P'-In	2.612(1)	In-C(41)	2.185(5)
P-Si(1)	2.262(2)		
P-Si(2)	2.261(3)		
(b) Bond angles			
In-P-In'	92.97(4)	C(31)-In-C(41)	105.7(2)
In-P-Si(1)	107.30(7)	P-Si(1)-C(11)	107.9(2)
In-P-Si(2)	120.62(8)	P-Si(1)-C(12)	111.0(3)
In'-P-Si(1)	112.32(8)	P-Si(1)-C(13)	108.8(3)
In'-P-Si(2)	114.64(7)	P-Si(2)-C(21)	107.1(3)
Si(1)-P-Si(2)	108.26(8)	P-Si(2)-C(22)	108.5(3)
P-In-P'	87.03(4)	P-Si(2)-C(23)	110.2(4)
P-In-C(31)	118.1(2)	In-C(31)-C(32)	118.2(5)
P-In-C(41)	114.3(2)	In-C(31)-C(36)	125.3(5)
P'-In-C(31)	112.7(1)	In-C(41)-C(42)	127.9(5)
P'-In-C(41)	118.8(2)	In-C(41)-C(46)	114.5(5)

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Table 3. Selected bond lengths (Å) and bond angles (°), with ESD's in parentheses, for  $[\text{Ph}_2\text{InAs}(\text{SiMe}_3)_2]_2$  (II).

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(a) Bond lengths

As(1)-In(1)	2.689(1)	As(2)-In(1)	2.689(1)
As(1)-In(2)	2.683(1)	As(2)-In(2)	2.682(1)
As(1)-Si(11)	2.344(4)	As(2)-Si(21)	2.370(4)
As(1)-Si(12)	2.352(2)	As(2)-Si(22)	2.353(2)
In(1)-C(1)	2.19(1)	In(2)-C(13)	2.17(1)
In(1)-C(7)	2.17(1)	In(2)-C(19)	2.17(1)

(b) Bond angles

In(1)-As(1)-In(2)	93.47(4)	In(1)-As(2)-In(2)	93.48(4)
In(1)-As(1)-Si(11)	119.8(1)	In(1)-As(2)-Si(21)	121.6(1)
In(1)-As(1)-Si(12)	110.3(1)	In(1)-As(2)-Si(22)	107.8(1)
In(2)-As(1)-Si(11)	118.2(1)	In(2)-As(2)-Si(21)	116.6(1)
In(2)-As(1)-Si(12)	107.5(1)	In(2)-As(2)-Si(22)	111.3(1)
Si(11)-As(1)-Si(12)	106.7(1)	Si(21)-As(2)-Si(22)	105.6(1)
As(1)-In(1)-As(2)	86.22(4)	As(1)-In(2)-As(2)	86.49(3)
As(1)-In(1)-C(1)	112.5(2)	As(1)-In(2)-C(13)	115.8(3)
As(1)-In(1)-C(7)	117.4(3)	As(1)-In(2)-C(19)	116.4(2)
As(2)-In(1)-C(1)	115.2(3)	As(2)-In(2)-C(13)	114.5(2)
As(2)-In(1)-C(7)	115.4(3)	As(2)-In(2)-C(19)	114.3(3)
C(1)-In(1)-C(7)	108.9(3)	C(13)-In(2)-C(19)	108.2(3)
As(1)-Si(11)-C(111)	109.8(4)	As(2)-Si(21)-C(211)	111.3(5)
As(1)-Si(11)-C(112)	108.8(5)	As(2)-Si(21)-C(212)	106.6(5)
As(1)-Si(11)-C(113)	106.5(5)	As(2)-Si(21)-C(213)	107.7(5)

Table 3 (cont.)

## (b) Bond angles (cont.)

As(1)-Si(12)-C(121)	106.3(4)	As(2)-Si(22)-C(221)	108.7(4)
As(1)-Si(12)-C(122)	111.0(4)	As(2)-Si(22)-C(222)	110.6(4)
As(1)-Si(12)-C(123)	109.6(4)	As(2)-Si(22)-C(223)	107.7(4)
In(1)-C(1)-C(2)	123(1)	In(2)-C(13)-C(14)	126(1)
In(1)-C(1)-C(6)	119(1)	In(2)-C(13)-C(18)	119(1)
In(1)-C(7)-C(8)	117(1)	In(2)-C(19)-C(20)	119(1)
In(1)-C(7)-C(12)	125(1)	In(2)-C(19)-C(24)	125(1)

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